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System Design

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AUTOMATED CRYOGENIC SAMPLING AND GAS CHROMATO-
GRAPHIC ANALYSIS OF AMBIENT VAPOR-PHASE ORGANIC
COMPOUNDS: SYSTEM DESIGN

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An automated system for unattended repetitive sampling and analysis of volatile organic compounds has been designed and a prototype constructed. The sampling/analysis scheme involves reduced temperature preconcentration of analytes from whole air with subsequent thermal desorption and capillary column gas chromatographic analysis. This paper presents the hardware configuration, timing cycles and overall functional integration of the system. The compact sample collection/injection package is described and data are given to show temperature change rates and plateau stability for the various heated and cooled analytic zones. The system is based on modified commercially available equipment and is ultimately intended for semi-real time monitoring from a manifold or as a centrally located laboratory instrument for analyzing air samples collected in the field.

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AUTOMATED CRYOGENIC SAMPLING AND GAS CHROMATOGRAPHIC ANALYSIS OF AMBIENT VAPOR-PHASE ORGANIC COMPOUNDS: SYSTEM DESIGN

Introduction

The U.S. Environmental Protection Agency (EPA) is currently developing analytical methodology for the measurement of volatile organic compounds (VOC's) present in ambient air. Since these compounds typically occur in great numbers, yet individually in low concentrations (often less than 1 ppb by volume),^{1,2} their identification and quantitation become a non-trivial task. One particular analysis approach is to pull whole air through a reduced temperature trap to condense target compounds onto trap surfaces and then, by rapid heating, inject the concentrated sample mixture into a gas chromatograph (GC) for analysis.^{3,4,5} The analysis portion of this technique is accomplished with state-of-the-art GC separation methods including oven temperature programming and appropriate combinations of detectors and high resolution capillary columns.^{6,7} Reduced temperature concentration, however, poses some questions, particularly with respect to trapping low boiling point VOC's without also trapping major constituents of air.

The suitability of reduced temperature preconcentration for a particular analyte can be estimated by extrapolations of known vapor pressure versus temperature data in the form of Clausius-Clapeyron equations.⁸ Such curves extended down to a lowest useable temperature of -183°C (boiling point of oxygen) indicate trapping capability to sub-ppb levels for all compounds on a list of VOC's selected for analysis.⁹ Table 1 lists these compounds of interest along with data and approximations of vapor pressures at relevant temperatures.^{10,11,12} Laboratory experiments with a selection of these compounds have verified collection-release efficiencies near 100%.¹³

Two other issues associated with cryogenic preconcentration from whole air are trap clogging due to ice formation and analyte reaction with co-collected compounds such as ozone (O_3) and nitrogen dioxide (NO_2). These topics are being investigated at Battelle Laboratories, Columbus, OH, under EPA contract 68-02-3487, as part of a research effort co-ordinated with this work. Preliminary experiments performed at Battelle indicate that Nafion (Dupont Company, Wilmington, DE) tubing dries air effectively, yet passes all compounds that were tested and that artifacts due to reactions of analytes trapped together with typical ambient concentrations of O_3 and NO_2 are negligible.¹⁴ A final problem area, the co-collection of ambient particles, can be avoided with an appropriate inlet-manifold and filtration system.

The scope of this paper is restricted to the hardware configuration and its functional integration to implement an automated system based on the techniques mentioned above. Details concerning calibration, data quality assurance, chemistry of trapping and analysis and data interpretation will be addressed elsewhere. The major objective, automated repetitive operation, is accomplished with a microprocessor-based GC and a commercially available (but significantly modified) cryogenic trapping and desorption instrument. The main effort is directed toward the design and testing of a sample handling package to be physically and functionally compatible with the injection or auxiliary zone of the GC. The trap design is optimized for rapid heating and cooling, yet great care is taken to assure that trap and GC oven cooling does not impact the temperature of the other components. In addition, a programming sequence for repeated automated sampling and analysis is developed

that allows for collection of the next sample during the analysis run of the current sample. Finally, the sampling package is constructed with a duplicate sampling stream, which can be used for simultaneous replicate analyses with the addition of another column and detector.

Experimental Equipment

The prototype system is a composite of two instruments, a Hewlett-Packard model 5880A-Level 4 Gas Chromatograph¹⁵ and a Nutech model 320-01 Cryogenic sampling unit.¹⁶ The GC has the capability to separate and quantify the compounds in question with an analysis procedure specified by Battelle Laboratories.¹³ This procedure requires a high resolution capillary column, (SE-54 WCOT), a temperature programmed analysis run (3 min at -50°C, then 8°/min up to 150°C, then 7 min at 150°C), and both flame ionization and electron capture detectors (FID and ECD). Protection of the analytes also requires that transfer components (tubing, valves) be heated (at least 50°C in the prototype system) to maintain sample integrity and that the trap be heated rapidly during injection to optimize chromatographic resolution, particularly for the more volatile compounds. A final consideration is the minimization of trap cool-down time after injection to allow a fast re-start of the sample collection cycle.

The Nutech instrument consists of two subsystems, an electronics console for monitoring, setting, and controlling temperatures, and a sample handling unit containing the trapping and injection plumbing. In response to a signal from the GC's microprocessor, the console changes the sampling mode (collection or injection) by switching the flow configuration of a multiport valve. The temperature of the sample trap is controlled during collection by regulating the release of liquid nitrogen into the trap enclosure and during injection by passing current through a heating element in contact with the trap. Two other controlling channels are available for independently heating sample lines and valves. All temperatures, which are manually preset and automatically stabilized at their setpoints, can be monitored on a digital display. The sampling subsystem normally supplied by Nutech is intended for analyzing solid sorbent cartridges and, therefore, has been replaced with a package specifically designed for our application.

Hardware Design

The heart of the sampling system is the cryogenic trap. The main criteria for the design, rapid heating, and cooling were met by winding the trap tubing around a hollow cylindrical 250-watt heater and enclosing this assembly with a stainless steel shell. Direct thermal contact between the heater and trap tubing assures rapid heating (-155°C to +100°C in 55 sec) and the shell facilitates efficient cooling (+122°C to -155°C in 225 sec) by confining the cryogen to the small air volume surrounding the trap assembly. The shell incorporates metal fittings for the coolant inlet and vent and is insulated with heat resistant sealant. Figure 1 shows a disassembled trap enclosure. Note that the shell consists of two pieces for easy access to the trap tubing and that small 25-watt cartridge heaters (and their heat sinks) are attached to the trap inlet and outlet tubing protruding from the shell. These provide a heat source and thermal inertia to eliminate "cold" spots in the transfer tubing. Note also that the enclosure contains two independent trapping tubes for possible replicate analyses.

TABLE 1. VOC's SELECTED FOR ANALYSIS AND THEIR APPROXIMATE PRESSURES

Compound Name	Chemical Formula*	Vapor Pressure at 0°C (mm Hg)	Vapor Pressure at -183°C (atm)**
Acrylonitrile (vinylcyanide)	$\text{CH}_2 = \text{CH} - \text{C} = \text{N}$	88 [‡]	5.3×10^{-18}
Benzene	C_6H_6	25 [‡]	6.6×10^{-18}
Benzylchloride (α -chlorotoluene)	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	0.23**	2.3×10^{-22}
Carbon tetrachloride	CCl_4	32 [‡]	1.3×10^{-18}
Chlorobenzene (phenylchloride)	$\text{C}_6\text{H}_5\text{Cl}$	2.6 [‡]	1.4×10^{-18}
Chloroform (trichloromethane)	CHCl_3	60 [‡]	4.7×10^{-14}
1,2-dibromoethane	$\text{CH}_2\text{BrCH}_2\text{Br}$	3.8 [‡]	4.8×10^{-18}
1,2-dichloroethane (ethylenedichloride)	$\text{CH}_2\text{ClCH}_2\text{Cl}$	24 [‡]	3.6×10^{-18}
1,1-dichloroethylene (vinylidenechloride)	CH_2CCl_2	205**	5.3×10^{-13}
1,3-dichloropropene	$\text{CHCl} = \text{CHCH}_2\text{Cl}$	—	—
Ethylene oxide	$\text{CH}_2\text{CH}_2\text{O}$	> 760*	6.1×10^{-12}
Hexachlorobutadiene	$\text{Cl}_2\text{CCCICCCl}_2$	—	—
Methylchloroform (1,1,1-trichloroethane)	CCl_3CH_3	35**	4.5×10^{-18}
Pyridine	CHCHCHCHCHN	4.1 [‡]	1.2×10^{-18}
Tetrachloroethylene	CCl_2CCl_2	4.2 [‡]	5.6×10^{-18}
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	6.9 [‡]	5.5×10^{-18}
Trichloroethylene	$\text{CCl}_2 = \text{CHCl}$	23 [‡]	8.4×10^{-18}
1,1,2-trichloro-1,2,2-trifluoroethane	$\text{CFCl}_2\text{CF}_2\text{Cl}$	99**	3.6×10^{-13}
Vinyl chloride (chloroethylene)	CH_2CHCl	> 760 [‡]	1.4×10^{-10}
o-Xylene (1,2-dimethylbenzene)	$(\text{CH}_3)_2\text{C}_6\text{H}_4$	1.5 [‡]	1.1×10^{-18}

*Data from Verschueren (1977).

**Approximated using Clausius-Clapeyron equations and parameters from Handbook of Chemistry and Physics (1973).

†Data from Jordan (1954).

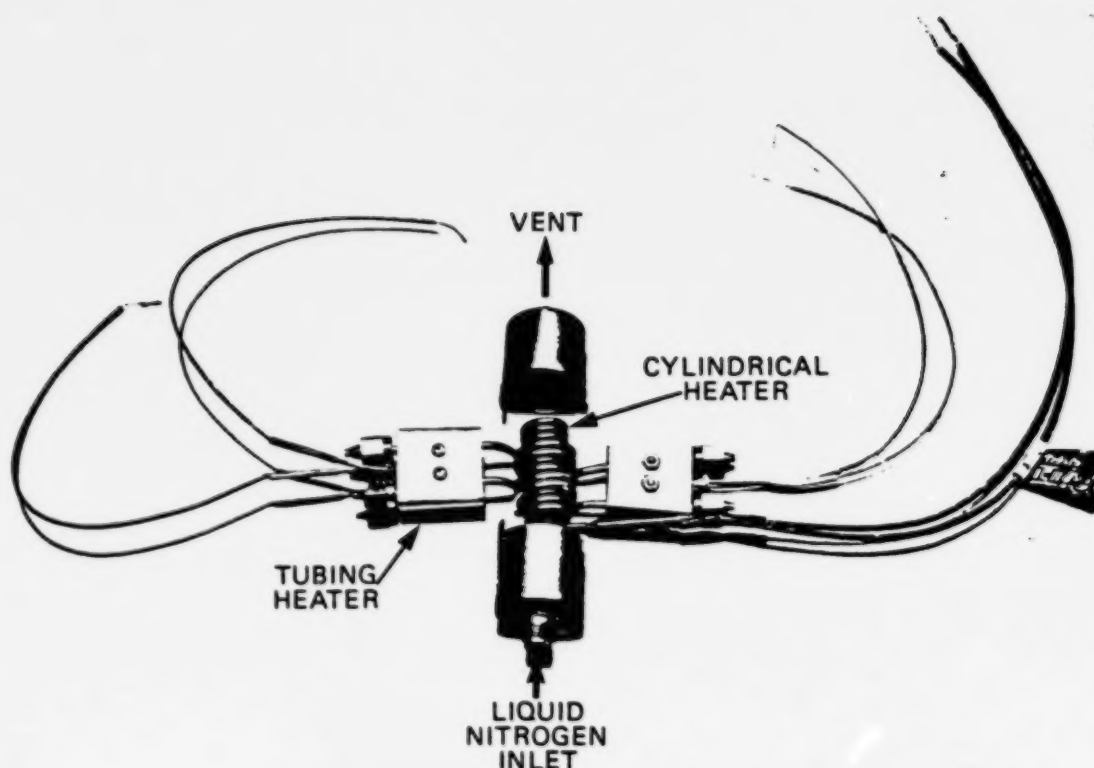


Figure 1. Photograph of trap assembly with opened two-piece shell.

The sampling mode is controlled by a six-port air actuated valve. During sample collection, ambient air is routed from the manifold to the valve, then through the cold trap, back to the valve and out to a vent, while the carrier gas flows through the valve directly to the column. During injection mode, however, the carrier is routed from the valve through the trap, back to the valve and then to the column, while the ambient air is shunted aside. A flow schematic of this arrangement is given in Figure 2.

The final configuration of the sample handling hardware (see Figure 3) includes two valves, two traps, and related tubing to keep available the option for replicate analyses. These are mounted on a baseplate which is fitted into the injection/auxiliary zone of the GC directly above (but insulated from) the column oven. The injection end of the column is brought up from the oven through this plate and joined to the carrier gas line with a zero dead volume connector. The valves and all sampling lines are maintained near 70°C with cartridge or rope heaters controlled by the Nutech instrument. The small cartridge heaters near the trap enclosure are maintained at a minimum of 85°C with an externally mounted variac. As can be seen in Figure 3, only one sample stream is currently in use. During normal operation, a 6" x 6" x 9" aluminum box is fitted over the sample handling elements to complete the package. Trap coolant is vented through the top of the box.

Event Sequencing

The sampling and analysis sequence accounts for all hardware limitations and timing requirements yet optimizes time coverage by allowing the next

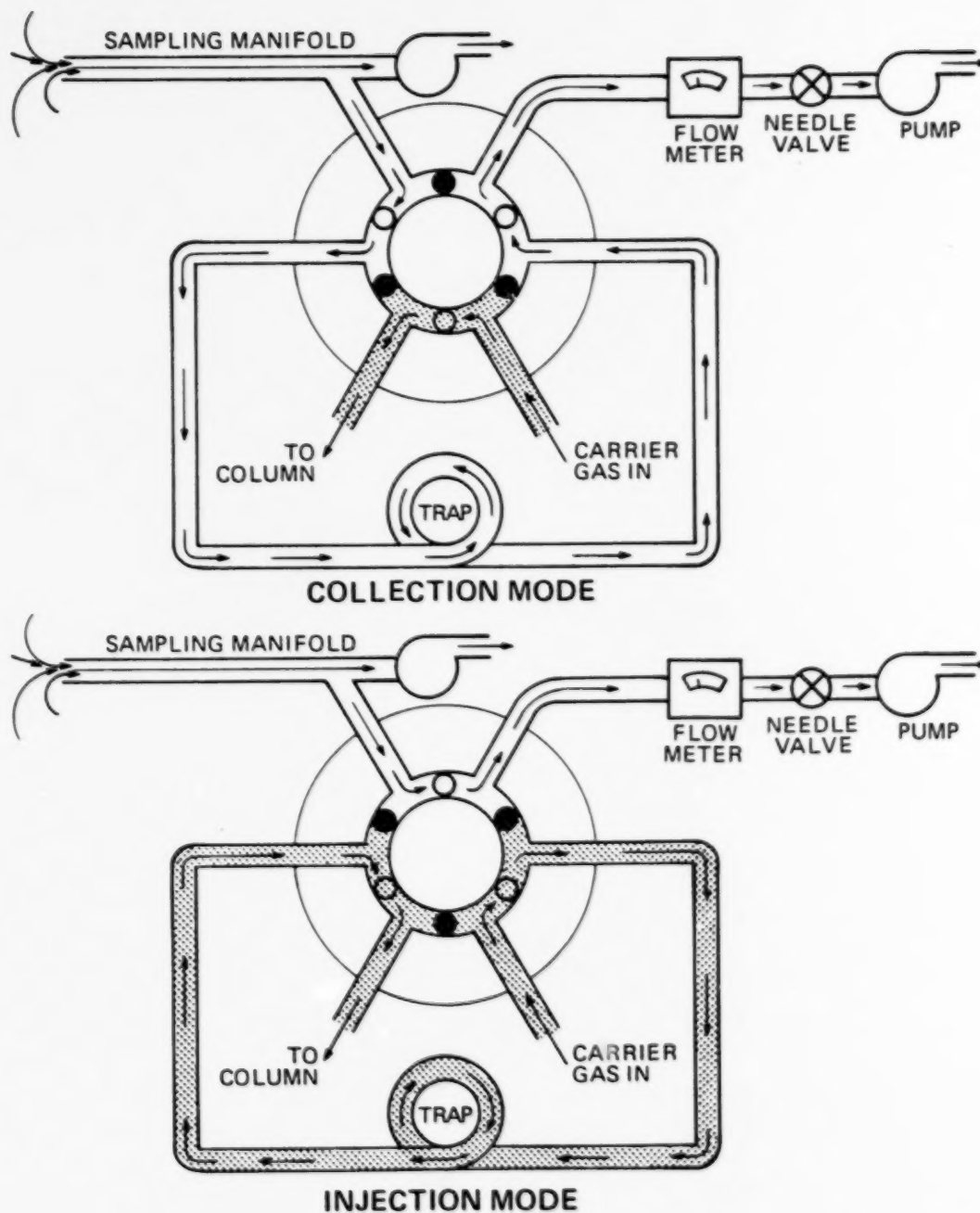


Figure 2. Flow path schematic showing cross-section of a six-port sampling valve in collection and injection mode.

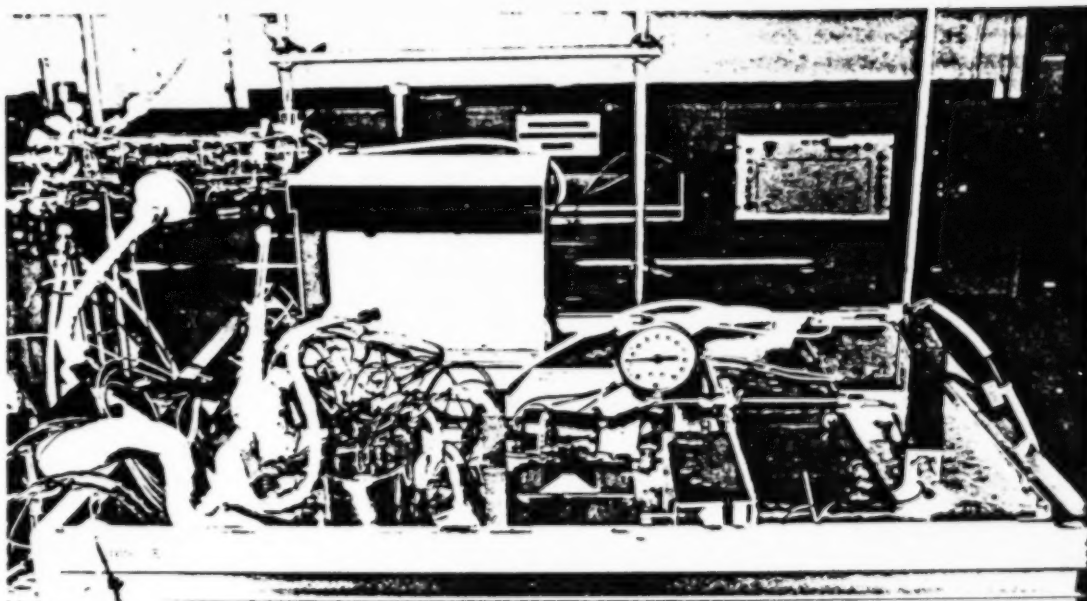


Figure 3. Photograph of the sample handling package installed in the injection/auxiliary zone of the GC.

sample to be collected during the current analysis. Time coverage is defined as the ratio of sample collection time to total run time. In this case, total run time is composed of the 35-min analysis (defined earlier in terms of an oven temperature program) plus a 10-min "post-run" time between analyses, during which oven temperature is reset and the data report is printed. Sample collection is suspended only during injection mode (length of 9.5 min) when the trap is heated and then cooled back to trapping temperature. Thus, with these constraints, a single trap-column-detector system can sample 35.5 min out of a 45-min run for a time coverage of 79%.

A master timing diagram is presented in Figure 4. The trap and oven temperature graphs are real traces made with calibrated Type K thermocouples imbedded in the respective temperature zones. Time scales indicating both real time and analysis run time are shown along with timing step functions that mark sampling valve mode (injection or collection) and GC mode (analysis or reset). Note that the times allowed for trap and oven temperature reset are quite generous. This way, changes in these temperature setpoints will not require alterations in the overall program.

Results

Results for typical repetitive system operation are presented in Figure 4. After an initial turn-on procedure, during which the operator presets various temperatures and establishes the necessary gas flows, the prototype system can perform automated sampling and analysis without intervention

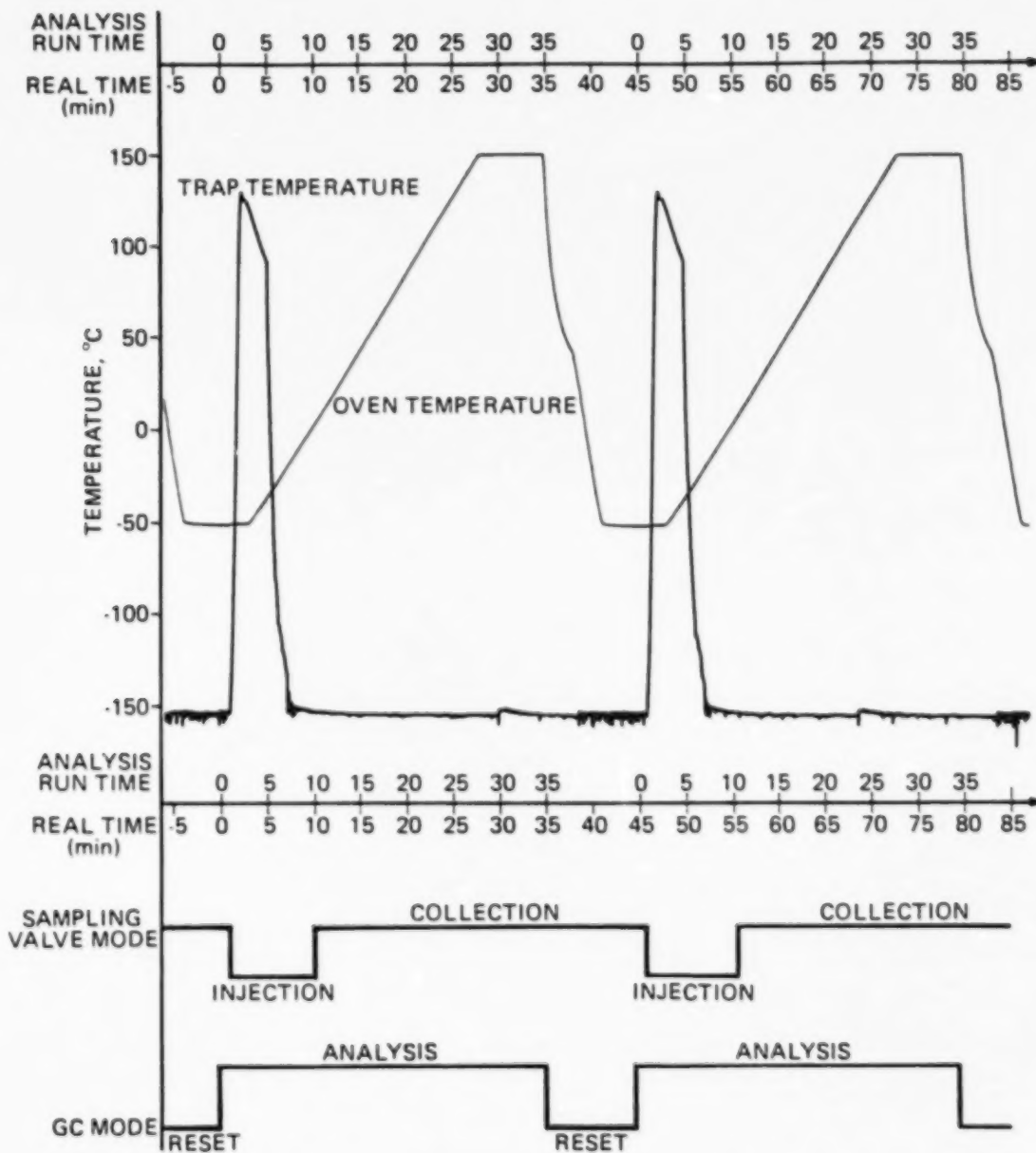


Figure 4. Time dependent sequencing and temperature charts for a typical set of repeated sampling/analysis runs.

until some external support fails. Typically, the limiting factor is the liquid nitrogen supply that furnishes cooling for both the GC oven and the sampling trap. A 160-liter dewar at 10 to 20 psig is usually sufficient for about 28 consecutive 45-min runs.

The trap enclosure and the GC oven (which both cycle to low temperatures) are by necessity located very close to sample handling elements that require heating to maintain sample integrity. In order to monitor the temperature variations during a full run, thermocouples were placed in contact with various potential trouble spots within the sampling package. The regions controlled by the Nutech instrument remained exactly at the preset temperatures, i.e., valve block at 70°C and sample lines at 75°C. The valve tubing to GC column connector, which was heated only by two turns of a flexible resistance element, ranged between 50 and 60°C, depending on oven temperature. The small 25-watt elements just outside the trap enclosure maintained the outlet tubing between 85 and 125°C. The air temperature at the geometric center of the covering box remains unperturbed at 52°C. Thus, the 50°C minimum temperature criterion for sample handling elements is met. The thermocouples were permanently installed to allow periodic checks.

Trap temperature stability during a run was measured for trapping temperatures ranging from 50°C down to -180°C. From +50 to -70°C, trap temperature stayed at the preset value, but temperature excursion about the nominal value increased monotonically to a maximum of $\pm 4^\circ\text{C}$ at a set point of -180°C. Close examination of the thermocouple trace of trap temperature in Figure 4 shows the fluctuations about the setpoint of -155°C to be about $\pm 3^\circ\text{C}$. Since these trapping temperature changes are relatively small and occur rapidly compared to the total trapping time, they should not appreciably affect the performance of the trap. As can also be seen in Figure 4, oven temperature during a programmed run has no apparent error.

Conclusions and Recommendations

The prototype system described above performs unattended repetitive sampling and analysis precisely as intended. The system successfully incorporates the multiple channel temperature control capability of a commercially available instrument with a custom built sample handling package that is physically integrated into a microprocessor-controlled GC. Software-based sequencing, which coordinates and controls all phases of operation, allows overlapping sampling and analysis functions to optimize time coverage.

Ongoing development efforts for the system include: 1) installation of a second column and detector for replicate analyses, 2) automation of a calibration and purge system, 3) implementation of automated data processing, and 4) installation of the whole system in a mobile laboratory. Tests are currently being conducted to provide statistical comparisons of run-to-run chromatographic results and to gain insight into the effects of using different trapping temperatures and trap materials.

We feel that system automation offers a number of advantages, primarily that data quality is enhanced by eliminating the small differences in repetitive procedures which require the periodic intervention of an otherwise underutilized operator. Also, prolonged around the clock field monitoring (with a mobile version of the system) would require very little dedicated manpower and, thus, make semi-real time sampling more cost-effective.

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References

1. T.E. Gradel, Chemical Compounds in the Atmosphere, Academic Press, Inc., New York, 1978.
2. H.B. Singh, L.J. Salas, H. Shigeishi, and E. Scribner, "Atmospheric halocarbons, hydrocarbons, and sulfur hexafluoride: global distribution, sources, and sinks," Science, 203 : 899-903 (1979).
3. T.A. Bellar, M.F. Brown, and J.E. Sigsby, Jr., "Determination of atmospheric pollutants in the parts-per-billion range by gas chromatography - a simple trapping system for use with flame ionization detectors," Anal. Chem., 35 : 1924-1927 (1963).
4. W.A. Lonneman, S.L. Kopczynski, P.E. Darley, and R.D. Sutterfield, "Hydrocarbon composition of urban air pollution," Envir. Sci. Technol., 8 : 229-235 (1974).
5. R.A. Rasmussen, D.E. Harsch, P.H. Sweany, J.P. Krasner, and D.R. Cronn, "Determination of atmospheric halocarbons by a temperature-programmed gas chromatographic freezeant concentration method," JAPCA 27: 579-581 (1977).
6. High Resolution Gas Chromatography, 2nd. ed., R.R. Freeman, editor, Hewlett-Packard Co., 1981.
7. H.B. Singh, L.J. Salas, R. Stiles, and H. Shigeishi, "Measurements of Hazardous Organic Chemicals in the Ambient Atmosphere," SRI Final Report on EPA contract #805990, Stanford, Calif. (1982).
8. P.L. Hanst, L.L. Spiller, D.M. Watts, J.W. Spence, and M.F. Miller, "Infrared measurement of fluorocarbons, carbon tetrachloride, carbonyl sulfide, and other atmospheric trace gases," JAPCA 25: 1220-1226 (1975).
9. J.D. Pleil, "Automated Cryogenic Sampling and Gas Chromatographic Analysis of Ambient Vapor-Phase Organic Compounds: Preliminary Design," Technical Note # ES-TN-82-02, Northrop Services Inc., Research Triangle Park, NC (1982).
10. Handbook of Chemistry and Physics, 54th ed., Robert C. Weast, editor, The Chemical Rubber Co. Press, Cleveland, Ohio, 1973 (pp. D-162-181).
11. T.E. Jordan, Vapor Pressure of Organic Compounds, Interscience Publishers Inc., New York, 1954.
12. K. Verschueren, Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Co., Atlanta, Ga, 1977.

13. M.W. Holdren and R.N. Smith, "Investigation of Cryogenic Sampling Techniques (Laboratory Experiments)", unpublished final report submitted to EPA 5/82, Contract #68-02-3487, Phase 1, Battelle Columbus Laboratories, Columbus, Ohio (1982).
14. M.W. Holdren, "Eighth Monthly Technical Progress Report: Evaluate Cryogenic Trapping as a Means for Collecting All Organic Compounds in Ambient Air", submitted to EPA 12/1982, Contract #68-02-3487, Work Assignment #14, Battelle Columbus Laboratories, Columbus, Ohio (1982).
15. Technical Manual : HP-5880A Gas Chromatograph, Hewlett-Packard Corp., Avondale, Pa, 1982.
16. Technical Manual : Nutech 320-01 Thermal Desorption System, Nutech Corp., Durham, NC, 1982.